

## English Translation

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(54) ADDITION REACTION-CURED SILICONE SPONGE RUBBER MOLDED BODY HAVING RESIN SKIN AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a silicone sponge rubber molded body having a resin skin excellent in strengths and abrasion resistance, and a method for manufacturing the same.

SOLUTION: The silicone sponge rubber molded body having the resin skin is composed such that the resin skin of an aqueous resin is laminated on the surface layer of the addition reaction-cured silicone sponge rubber molded body containing an emulsifier and a water-soluble polymer. This method for manufacturing the silicone sponge rubber molded body having the resin skin comprises coating the surface layer of the addition reaction-cured silicone sponge rubber molded body containing the emulsifier and the water-soluble polymer with the aqueous resin, and then drying the aqueous resin to form the resin skin.

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**CLAIMS****[Claim(s)]****[Claim 1]**

A silicone sponge rubber Plastic solid which has resin membrane, wherein resin membrane of aqueous resin is laminated by surface of an emulsifier and an addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer.

**[Claim 2]**

A silicone sponge rubber Plastic solid which has the resin membrane according to claim 1 forming from an addition reaction hardening type aqueosity silicone emulsion in which an addition reaction hardening type silicone sponge rubber Plastic solid contains an emulsifier and water-soluble polymer.

**[Claim 3]**

A silicone sponge rubber Plastic solid which has the resin membrane according to claim 1, wherein aqueous resin is what is chosen from a group which consists of aqueosity urethane system resin, aqueosity acrylic resin, and an aqueosity fluoro-resin.

**[Claim 4]**

Claim 1, wherein aqueous resin is hardenability - a silicone sponge rubber Plastic solid of Claim 3 given in any 1 clause.

**[Claim 5]**

A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane applying aqueous resin to an addition reaction hardening type silicone sponge rubber Plastic solid surface containing an emulsifier and water-soluble polymer, drying this aqueous resin after an appropriate time, and forming resin membrane.

**[Claim 6]**

A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane according to claim 5 forming from an addition reaction hardening type aqueosity silicone emulsion in which an addition reaction hardening type silicone sponge rubber Plastic solid contains an emulsifier and water-soluble polymer.

**[Claim 7]**

A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane according to claim 5, wherein aqueous resin is what is chosen from aqueous urethane resin, an aqueosity acrylic resin, or an aqueosity fluoro-resin.

**[Claim 8]**

A manufacturing method of Claim 5, wherein aqueous resin is hardenability - a silicone sponge rubber Plastic solid of Claim 7 given in any 1 clause.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to an addition reaction hardening type silicone sponge rubber Plastic solid which has resin membrane, and a manufacturing method for the same.

[Background of the Invention]

[0002]

The outstanding buffer nature and vibration proof are evaluated and silicone sponge rubber is widely used for sporting gear, an INSHU letter, etc. Since various characteristics, such as pliability, elasticity, firmness, and feel nature, are provided, it may be used for the putt for ready figures which modeled form on the female udder the puff for makeup, and aimed at obtaining the ready figure. It excels in heat resistance and weatherability, and since it is lightweight, taking advantage of this characteristic, it is used as a surface coating material; structural fixed form sealant of part; copying machine rolls, such as packing, a gasket, and an O ring, etc. Conventionally, many constituents are proposed for [ this ] silicone rubber sponge formation as follows. For example, the silicone rubber sponge plasticity constituent which blends the pyrolysis type organic blowing agent represented by azobisisobutyronitrile is taught to JP,44-461,B and JP,7-247436,A.

A coat is thermoplastics and the silicone rubber sponge plasticity constituent which blends the balloon which included volatile hydrocarbon like butane or isobutane is proposed by JP,5-209080,A. In JP,54-135865,A and JP,5-70692,A. It consists of the water or alcohol, and the platinum system catalyst of alkenyl-group content diorganopolysiloxane, the ORGANO hydrogen polysiloxane, and a small quantity, The silicone rubber sponge plasticity constituent made to foam with the hydrogen gas emitted at the reaction of this ORGANO hydrogen polysiloxane and water is taught.

The emulsion which becomes JP,7-122000,B from organopolysiloxane, an emulsifier, water, and a viscous agent is contained as a foaming agent, The silicone rubber sponge plasticity constituent made to foam using evaporation of water and expansion is taught, and to JP,2002-114860,A.

Hydrosilylation reaction cross-linking which consists of alkenyl-group content diorganopolysiloxane, an ORGANO hydrogen polysiloxane, and a platinum system catalyst, That is, it is an addition reaction hardening setup-of-tooling product, and the silicone rubber sponge plasticity constituent containing the water-absorbent-polymer powder containing water is taught.

However, the problem of being hard to become is among the sponge which has a fine cell of what can form a complicated-shaped three-dimensional Plastic solid from these silicone rubber sponge plasticity constituent.

Then, this invention persons invented and did patent application about the method of manufacturing silicone rubber sponge, from the addition reaction hardening type aqueous silicone emulsion containing an emulsifier and water-soluble polymer (application for patent 2002-311470).

[0003]

However, the thing which has that possible the silicone sponge rubber produced from the emulsion for addition reaction hardening type silicone rubber sponge containing an emulsifier and water-soluble polymer forms a complicated-shaped three-dimensional Plastic solid, the mechanical strength of the acquired Plastic solid is low -- moreover -- the surface -- a scratch -- scratching -- etc. -- he has noticed that there is a problem of being easy to be damaged by a physical impact. It is publicly known one (refer to JP,59-37580,A) to coat the surface of silicone rubber sponge with room-temperature-vulcanization type silicone rubber, and to protect this surface, Coating the surface of an emulsifier and the addition reaction hardening type silicone rubber sponge containing water-soluble polymer with room-temperature-vulcanization type silicone rubber is happening to think easily, if it is a person skilled in the art. However, in order to coat uniformly the surface of an emulsifier and the addition reaction hardening type silicone rubber sponge containing water-soluble polymer with room-temperature-vulcanization type silicone rubber, it is necessary to melt and coat organic solvents, such as toluene, with room-temperature-vulcanization type silicone rubber, and is not desirable on safety and hygiene. even if it can coat -- a scratch -- scratching -- etc. -- it is insufficient for protecting from damage by a physical impact.

[0004]

[Patent documents 1] JP,S44-461,B

[Patent documents 2] JP,H7-247436,A

[Patent documents 3] JP,H5-209080,A

[Patent documents 4] JP,S54-135865,A

[Patent documents 5] JP,H5-70692,A

[Patent documents 6] JP,H7-122000,B

[Patent documents 7] JP,2002-114860,A

[Patent documents 8] JP,S59-37580,A

[Description of the Invention]

[Problem to be solved by the invention]

[0005]

then -- this invention persons compensate the shortage of a mechanical strength of an addition reaction hardening type silicone rubber sponge Plastic solid -- a scratch -- scratching -- etc. -- it inquired wholeheartedly that the addition reaction hardening type silicone rubber sponge Plastic solid protected from damage by a physical impact should be developed, and this invention was reached.

the purpose of this invention compensates the shortage of a mechanical strength of an addition reaction hardening type silicone rubber sponge Plastic solid -- a scratch -- scratching -- etc. -- providing the addition reaction hardening type silicone rubber sponge Plastic solid which is hard to damage even if it receives a physical impact. And it is in providing the manufacturing method of this addition reaction hardening type silicone rubber sponge Plastic solid.

[Means for solving problem]

[0006]

These purposes, "(1) The silicone sponge rubber Plastic solid which has resin membrane, wherein the resin membrane of aqueous resin is laminated by the addition reaction hardening type silicone sponge rubber Plastic solid surface containing an emulsifier and water-soluble polymer.

(2) A silicone sponge rubber Plastic solid which has the resin membrane given in (1) forming from an addition reaction hardening type aqueous silicone emulsion in which an addition reaction hardening type silicone sponge rubber Plastic solid contains an emulsifier and water-soluble polymer.

(3) A silicone sponge rubber Plastic solid which has the resin membrane given in (1) being what chosen from a group which aqueous resin becomes from aqueous urethane system resin, aqueous acrylic resin, and an aqueous fluoro-resin.

(4) (1) - (3), wherein aqueous resin is hardenability is a silicone sponge rubber Plastic solid of a description either.

(5) A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane applying aqueous resin to an addition reaction hardening type silicone sponge rubber Plastic solid surface containing an emulsifier and water-soluble polymer, drying this aqueous resin after an appropriate time, and forming resin membrane.

(6) A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane given in (5) forming from an addition reaction type aqueous silicone emulsion in which an addition reaction hardening type silicone sponge rubber Plastic solid contains an emulsifier and water-soluble polymer.

(7) A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane given in (5) being what chosen from a group which aqueous resin becomes from aqueous urethane resin, an aqueous acrylic resin, and an aqueous fluoro-resin.

(8) either of (5) - (7), wherein aqueous resin is hardenability -- a manufacturing method of a silicone sponge rubber Plastic solid of a description. " -- it is attained.

[Effect of the Invention]

[0007]

The silicone sponge rubber Plastic solid which has the resin membrane of this invention, the resin membrane of aqueous resin -- excelling in a mechanical strength, since the hardening resin coat of aqueous hardening resin is preferably laminated by the surface of the silicone sponge rubber Plastic solid -- a scratch -- scratching -- etc. -- even if it receives a physical impact, it is hard to be damaged, namely, rubfastness is excellent.

According to the manufacturing method of the silicone sponge rubber Plastic solid which has the resin membrane of this invention. excelling in a mechanical strength -- a scratch -- scratching -- etc. -- it is hard to be damaged even if it receives a physical impact. The resin membrane of aqueous resin and the silicone sponge rubber Plastic solid in which the hardening resin coat of hardenability aqueous resin is preferably laminated by the surface of the silicone sponge rubber Plastic solid can be manufactured simply and efficiently.

[Best Mode of Carrying Out the Invention]

[0008]

The silicone sponge rubber Plastic solid which has the resin membrane in this invention, The resin membrane of aqueous resin is laminated by the surface of an emulsifier and the addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer, This resin membrane covered the surface of the addition reaction hardening type silicone sponge rubber Plastic solid, and has stuck thru/or pasted it up on the addition reaction hardening type silicone sponge rubber Plastic solid well.

An emulsifier and the addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer can take required form and size suitably according to uses, such as a sheet shaped, block like shape, a prismatic form, round bar shape, and the shape of a ball. It may be the coating membrane on other base materials, for example, textiles, a nonwoven fabric, glass crossing, a metal plate, and a plywood. the density which sorbo rubber usually has may be sufficient as the density -- 0.2 to 0.9 -- it is 0.4-0.7 preferably. Since the path of a cell inherent changes with the manufacturing method of an emulsifier and the addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer, Although it cannot generally specify, when manufactured stiffening the addition reaction hardening type aqueous silicone emulsion containing a following emulsifier and water-soluble polymer, heating subsequently, and drying, or by drying, making it heat and harden, it is 0.05-0.2 mm, for example. Of course, various sizes, such as 0.1-0.3 mm and 0.2-0.5 mm, and distribution can be taken. An emulsifier and the addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer, From the adhesion thru/or the adhesive viewpoint of resin membrane of aqueous resin, preferably an emulsifier 0.01 to 10 weight %, containing water-soluble polymer 0.01 to 15weight % -- yellowing at the time of heating -- it is good to contain water-soluble polymer for an emulsifier 0.01 to 2.5weight % 0.01 to 3weight %

preferably from a viewpoint of prevention.

[0009]

The manufacturing method of an emulsifier and the addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer, The addition reaction hardening type aqueous silicone emulsion which is not limited, for example, contains an emulsifier and water-soluble polymer especially can be stiffened, and it can manufacture heating subsequently and drying or by drying making it heat and harden.

The addition reaction hardening type aqueous silicone emulsion containing an emulsifier and water-soluble polymer, Although an ingredient top consists of the diorganopolysiloxane which has at least two alkenyl groups in the (A) one molecule at least, the organopolysiloxane which has (B) silicon atom absorbed water matter, (C) platinum system catalyst, the (D) emulsifier, (E) water solubility polymer, and (F) water, (A) The diorganopolysiloxane which has at least two alkenyl groups in one molecule, (B) By emulsifying the addition reaction hardening type liquid silicone rubber composition which consists of organopolysiloxane and (D) platinum system catalyst which have silicon atom absorbed water matter in the solution of (E) water solubility polymer with the (D) emulsifier, Or emulsify the diorganopolysiloxane which has at least two alkenyl groups in the (A) one molecule in the solution of (F) water solubility polymer with the (D) emulsifier, and subsequently, (B) It can manufacture by adding organopolysiloxane and (C) platinum system catalyst which have silicon atom absorbed water matter, and mixing.

[0010]

Here, the diorganopolysiloxane which has at least two silicon atom joint alkenyl groups in the (A) one molecule is base resin, and this alkenyl group carries out the addition reaction of it to this hydrogen atom of the organopolysiloxane which has silicon atom absorbed water matter, and constructs for it a bridge and hardens it.

As an alkenyl group, a vinyl group, an allyl group, and a propenyl group are illustrated. As organic groups other than an alkenyl group, although halo alkyl groups, such as aryl group; 3,3,3-trichloropropyl groups, such as alkyl-group; phenyl groups, such as a methyl group, an ethyl group, and a propyl group, and a tolyl group, and 3-chloropropyl group, are illustrated, a methyl group is preferred. The molecular structure for Motoshige may have preferred straight chain shape, and may be the chain branched slightly. Although the molecular weight in particular for Motoshige is not limited, it is preferred that the viscosity at 25 °C is 100 or more mPa-s and 100,000 mPa-s or less. The above-mentioned diorganopolysiloxane may use two or more sorts together.

[0011]

(B) Carry out the addition reaction of the organopolysiloxane which has at least two silicon atom absorbed water matter atoms in one molecule, and the silicon atom absorbed water matter atom constructs a bridge, and makes the silicon atom joint alkenyl group of diorganopolysiloxane (A) harden it under existence of a platinum system catalyst. Therefore, when diorganopolysiloxane (A) has two alkenyl groups, a part for Motoshige needs to have three or more silicon atom absorbed water matter atoms in one molecule. As a silicon atom joint organic group, although alkyl halide groups, such as aryl group; 3,3,3-trichloropropyl groups, such as alkyl-group; phenyl groups, such as a methyl group, an ethyl group, and a propyl group, and a tolyl group, and 3-chloropropyl group, are illustrated, a methyl group is preferred. Any, such as straight chain shape, branched, annular, and mesh shape, may be sufficient as the molecular structure for Motoshige. Although the molecular weight in particular for Motoshige is not limited, it is preferred that the viscosity at 25 °C is 1 or more mPa-s and 10 or 00 mPa-s or less. Especially if the mole ratio of the silicon atom joint alkenyl group in the silicon atom absorbed water matter atom in organopolysiloxane (B) and diorganopolysiloxane (A) is a range which both construct a bridge and harden and presents the shape of rubber, it will not be limited, but it is usually 0.5 to about three.

[0012]

(C) A platinum system catalyst is a catalyst which promotes the addition reaction to the silicon

atom joint alkenyl group in diorganopolysiloxane (A) of the silicon atom absorbed water matter atom in organopolysiloxane (B), The olefin complex of platinum impalpable powder, platinum black, chloroplatinic acid, and chloroplatinic acid, a complex compound with the alkenyl siloxane of chloroplatinic acid, a rhodium compound, and a palladium compound are illustrated. The amount used is sufficient quantity to construct a bridge, and promote and stiffen the addition reaction to the silicon atom joint alkenyl group in diorganopolysiloxane (A) of the silicon atom absorbed water matter atom in organopolysiloxane (B), and what is called a catalyst amount.

[0013]

(D) The diorganopolysiloxane to which an emulsifier has at least two silicon atom joint alkenyl groups in one molecule (A), (B) The organopolysiloxane which has at least two silicon atom absorbed water matter atoms in one molecule, Or the diorganopolysiloxane which has at least two alkenyl groups in the (A) one molecule, (B) It is blended in order to emulsify underwater the addition reaction hardening type liquid silicone rubber composition which consists of organopolysiloxane and (C) platinum system catalyst which have silicon atom absorbed water matter and to form a stable emulsion. If it excels in emulsification ability and an addition reaction is not checked, the kind in particular is not limited, but generally the emulsifier of a non-ion system is preferred. The non-ion system surface-active agent as an emulsifier of a non-ion system, Polyoxyethylene alkyl ether, polyoxyethylene phenyl ether, Ethylene glycol mono- fatty acid ester, propylene glycol mono- fatty acid ester, Sorbitan mono- fatty acid ester, sorbitan trifatty acid ester, polyoxyethylene mono- fatty acid ester, polio KISHIECHI range fatty acid ester, polyoxyethylene propylene glycol fatty acid ester, or a POE polyhydric alcohol class is illustrated. The HLB value of an emulsifier has a preferred thing of 4-14. An emulsifier may use two or more sorts together. The loadings of an emulsifier are 0.5 - 12 weight section more preferably 0.1 to 15 weight section to diorganopolysiloxane (A) 100 weight section. It is because the physical property of the silicone sponge rubber hardened and obtained tends to fall if the stable silicone emulsion cannot become easily if less than 0.1 weight sections, and 15 weight sections are exceeded.

[0014]

(E) When water-soluble polymer prepares an aqueosity silicone emulsion, while loss in quantity of the (D) emulsifier has an effect, concomitant use of water-soluble polymer and an emulsifier has a remarkable effect in the HAJIKI reduction at the time of applying aqueous resin to a silicone sponge rubber Plastic solid. As water-soluble polymer, alginic acid, sodium alginate, the sodium salt; methyl cellulose of carrageenan; carboxymethyl cellulose, Cellulose ether, such as ethyl cellulose and hydroxyethyl cellulose; denaturation starch, poly vinyl alcohol, sodium polyacrylate salt, and sodium salt polymethacrylate is illustrated. (E) Although it changes with kinds of water-soluble polymer, the content in solution is 0.5 to 3 weight % more preferably 0.1 to 5weight %. An emulsion low the viscosity of aqueous polymer solution and stable when there is less the quantity than 0.1 weight % is difficult to get, and when exceeding 5 weight %, viscosity is too high and it is because stirring may become difficult.

[0015]

(F) Water is a medium which makes the addition reaction hardening type liquid silicone rubber composition which consists of the above-mentioned ingredient (A), an ingredient (B), an ingredient (C) or an ingredient (A) - an ingredient (C) emulsify, if it is pure, it is good, and the kind is not restricted. Tap water, well water, ion exchange water, and distilled water are illustrated. The amount of the water used makes the addition reaction hardening type liquid silicone rubber composition which consists of the above-mentioned ingredient (A), an ingredient (B), an ingredient (C) or an ingredient (A) - an ingredient (C) emulsify, Especially if it is sufficient quantity to form silicone sponge rubber at the time of hardening, it will not be restricted, but it is 30 - 300 weight section preferably per diorganopolysiloxane (A) 100 weight section, and is 50 - 200 weight section more preferably. It is because the intensity of the silicone sponge rubber which will be formed if are hard to take the form of an aqueosity emulsion, it is, and there are things when less than 30 weight

sections, and 300 weight sections are exceeded may be spoiled.

[0016]

In this addition reaction hardening type aqueous silicone emulsion. In order to adjust mobility or to raise the mechanical strength of a hardened material, may blend various kinds of bulking agents, and as such a bulking agent, Precipitated silica, fumed silica, carbon black, pyrogenic silica, colloid calcium carbonate, Reinforcement nature bulking agents, such as fumed titanium dioxide; The end of quartz powder, diatomaceous earth, aluminosilicate, Un-reinforcing nature bulking agents, such as magnesium oxide and heavy calcium carbonate; what carried out hydrophobing processing of the silica filler of these with organic silicon compounds, such as dimethyldichlorosilane, hexamethyldisilazane, and octamethylcyclotetrasiloxane, is illustrated. In order to control hardening at ordinary temperature, it is preferred to blend an addition reaction depressant. Alcohols, paints, a heat-resistant agent, fire retardant, a plasticizer, an adhesion grant agent, etc. may be blended if needed.

[0017]

The diorganopolysiloxane which has at least two alkenyl groups in the (A) one molecule at least, (B) The addition reaction hardening type aqueous silicone emulsion which consists of the organopolysiloxane which has silicon atom absorbed water matter, (C) platinum system catalyst, the (D) emulsifier, (E) water solubility polymer, and (F) water can be manufactured, for example by the following methods.

(1) The diorganopolysiloxane (A) which has an alkenyl group of the specified quantity, How to feed into a high-speed-stirring mixer the solution of the organopolysiloxane (B) which has the silicon atom absorbed water matter of the specified quantity, the platinum system catalyst (C) of the specified quantity, and water-soluble polymer (E) of the specified quantity, and the emulsifier (D) of the specified quantity, and carry out predetermined time stirring mixing,

(2) The alkenyl group of the specified quantity. The addition reaction hardening type liquid silicone rubber composition which consists of the diorganopolysiloxane (A) which it has, organopolysiloxane (B) which has the silicon atom absorbed water matter of the specified quantity, and a platinum system catalyst of the specified quantity, the solution of water-soluble polymer (E) of the specified quantity, and the emulsifier (D) of the specified quantity. How to supply to a high-speed-stirring mixer and carry out predetermined time stirring mixing,

(3) The diorganopolysiloxane (A) which has an alkenyl group of the specified quantity, How to carry out [ feeds the solution of water-soluble polymer (E) of the specified quantity, and the emulsifier (D) of the specified quantity into a high-speed-stirring mixer, and ] stirring mixing of organopolysiloxane (B) and the platinum system catalyst (C) of the specified quantity which have the silicon atom absorbed water matter of the specified quantity after carrying out predetermined time stirring mixing.

In the above-mentioned manufacturing method, the diorganopolysiloxane (A) which has an alkenyl group is liquefied at ordinary temperature, and it is preferred to use it in the form of the liquid silicone rubber base which is the paste state thing which was mixed under a reinforcement nature silica filler and heating, and was prepared beforehand.

Although a homomixer, a paddle type mixer, a Henschel mixer, a HOMODI spar, a colloid mill, a vacuum mixing stirring mixer, etc. are illustrated as a mixer used here, if a stable emulsion is obtained, it will not be limited in particular.

[0018]

Degassing first is preferred while the addition reaction hardening type aqueous silicone emulsion containing this emulsifier and water-soluble polymer is involving in air bubbles at the time of agitation mixing. usually, although degassing comes out using a vacuum pump etc. in the state where it settled during stirring or into the container within the mixer and it carries out under decompression, neither a decompression degree nor degassing time in particular is limited, and should just continue degassing operation to the range without the existence of air bubbles visually.



Subsequently, it dries stiffening preferably 150 °C of addition reaction hardening type aqueous silicone emulsions containing an emulsifier and water-soluble polymer at the temperature of 50 to 120 °C from ordinary temperature, or hardening them, for example, and a silicone sponge rubber Mr. Plastic solid is formed. Subsequently, if this silicone sponge rubber Mr. Plastic solid is dried at 100 °C – 250 °C, water will be removed and a silicone sponge rubber Plastic solid will be formed. Since it may turn yellow at the time of stoving, after rinsing a silicone sponge rubber Mr. Plastic solid, it is preferred to carry out stoving.

Any, such as compression molding, injection moulding, extrusion molding, and coating, may be sufficient as the forming method.

[0019]

An emulsifier and the addition reaction hardening type silicone sponge rubber Plastic solid containing water-soluble polymer can be manufactured also an emulsifier, the addition reaction hardening type silicone rubber composition containing water-soluble polymer, and by stiffening an addition reaction hardening type liquid silicone rubber composition preferably.

[0020]

Since the silicone sponge rubber Plastic solid acquired in this way contains an emulsifier and water-soluble polymer, it has the feature of being hard to crawl aqueous resin, and the coating of aqueous resin is easy for it. Aqueous resin is the organic resin which distributed, emulsified or dissolved in water, and a thing which are hardenability organic resin preferably, and will form a firm coat if it heats or water evaporates. Especially, what it has a hydrophilic radical in a molecule, and particles are distributing underwater at colloid, and does not contain an emulsifier is preferred. Although aqueous urethane system resin, aqueous acrylic resin, aqueous polyester resin, aqueous EPOSHIKI resin, an aqueous fluoro-resin, aqueous silicone resin, aqueous polyethylene resin, especially these hardenability aqueous resin are specifically illustrated, Since it has rubber elasticity and the mechanical strength is excellent, the coat of aqueous urethane system resin is the most preferred, and subsequently aqueous acrylic resin and an aqueous fluoro-resin are preferred. When it mixes with what will be constructed for which a bridge and hardened if these aqueous resin is mixed with what will form a firm coat if moisture evaporates, the thing which has denaturalized by the special functional group and carries out self-bridge construction, and a cross linking agent, and a curing catalyst, there are some etc. which are constructed for which a bridge and hardened. A cross linking agent and/or a curing catalyst may be blended if needed, and an adhesive grant agent, colorant, fire retardant, an antiseptic, an antifungal agent, a little organic solvents, etc. may be blended further.

[0021]

The spreading to the silicone sponge rubber Plastic solid of aqueous resin can take various methods, such as impregnation, spray painting, \*\*\*\* coating, roller coating, and knife coating. The coverage of aqueous resin has a preferred quantity which serves as a range whose thickness of film after [ after air-drying at a room temperature ] stoving is 5 micrometers – 70 micrometers. Although it changes with elastic moduli of aqueous resin, if the thickness of the resin layer from aqueous resin is a range which are 5 micrometers – 100 micrometers, the pliability of a silicone sponge rubber Plastic solid will not be spoiled. the resin layer from aqueous resin -- the hardening resin film is preferably laminated by the whole surface of a silicone sponge rubber Plastic solid, or some fields. Some fields [ a part of ] may laminate.

[Working example]

[0022]

Hereafter, the working example and comparative example of this invention are hung up. There is a weight section among an working example and a comparative example with a part, it is weight % which is with %, and viscosity shows the numerical value in 25 °C. This invention is not limited by these working examples.

[0023]

Each characteristic in an working example and a comparative example was measured on condition of

the following.

Density of silicone sponge rubber: The silicone sponge rubber sheet was pierced to the punch of the constant diameter, the weight and thickness of the sheet piece which were pierced were measured, and weight/volume ( $\text{g}/\text{cm}^3$ ) was computed as density.

HAJIKI of aqueous resin: HAJIKI when the piece of a dumbbell of silicone sponge rubber was immersed in aqueous resin and taken out was observed visually.

Hardness of silicone sponge rubber: According to JIS K6253, it measured using low-pressure load machine CL-150 (made by polymer meter incorporated company) for rubber hardness meters.

Tensile strength of silicone sponge rubber: It measured according to JIS K6251.

The wear rate of the silicone sponge rubber which has resin membrane: SUGA abrasion testing machine NUS-ISO-1 (made by Suga Test Instruments Co., Ltd.) was used, and it measured by the reciprocating-movement attrition test method. The roll kneader which stuck the abrasive paper of the particle size 1200 was rotated 30 times on the silicone sponge rubber sheet as 50g of loads. (Sample weight after front [ wear ] sample weight (mg)-wear (mg)) The sample weight before  $\times 100$  /wear was computed as a wear rate. The sample weight before wear was found by measuring the weight of the specimen which consists of the roll kneader touch area (30mmX15mm) and thickness (about 2 mm) of a silicone sponge rubber sheet.

[0024]

The ingredient used by the working example and the comparative example is as follows.

A-1: The chain both ends of viscosity 10,000 mPa-s 17 copies of hydrophobic fumed silica of specific surface area  $2$  [ of 200 m ]/g by which the surface treatment was carried out to 100 copies of dimethylpolysiloxane (0.14% of vinyl group content) blocked by the dimethylvinyl siloxy group by hexamethyldisilazane. Liquid liquid silicone rubber base which was mixed uniformly and prepared by performing heat treatment for 2 hours at 180 \*\*;

A-2: The viscosity 40, Aerosil R-972 which is the fumed silica by which the surface treatment was carried out to 100 copies of dimethylsiloxane methylvinyl siloxane copolymers (0.14% of vinyl group content) by which chain both ends of 000 mPa-s were blocked with a trimethylsiloxy group by dimethyldichlorosilane. (Product made from Japanese Aerosil, Inc.) A liquid liquid silicone rubber base which mixed 17 copies uniformly and was prepared by performing heat treatment for 2 hours at 180 \*\*;

B: A both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of viscosity 5 mPa-s (0.8% of silicon atom absorbed water matter content);

C: A complex of chloroplatinic acid and divinyl tetramethyl disiloxane;

D: All [ 3,5-dimethyl- 1-hexyne-3 ] as an addition reaction retardant;

E-1: Solution of sodium polyacrylate which is water-soluble polymer (1% of water-soluble polymer content);

E-2: Solution of sodium salt of carboxymethyl cellulose which is water-soluble polymer (3% of water-soluble polymer content)

E-3: Water made to gel by an acrylate polymer partial sodium salt bridge construction thing which is a water-absorbent polymer (0.3% of water-absorbent-polymer content);

E-4: Ion exchange water

F-1: Polyoxyethylene dioleate (HLB value 10.4);

F-2: Poxoxyethylene dilaurate (HLB value 6.6);

F-3: Poxoxyethylene lauryl ether (HLB value 9.6);

F-4: Higher alcohol system non-ion system surface-active agent Selected Special Wax SS-50 (made by SANYO CHEMICAL INDUSTRIES LTD.) (HLB value 10.5);

F-5: Higher alcohol system non-ion system surface-active agent Selected Special Wax SS-70 (made by SANYO CHEMICAL INDUSTRIES LTD.) (HLB value 12.8);

G: Aquosity polyester system urethane resin "hide run HW-311" (it is aqueous urethane resin of a

dissolution thru/or what is called colloidal dispersion type [ underwater ] extremely distributed in the shape of a particle in urethane resin which has ionicity, i.e., an ion group whose urethane ionomer is the hydrophilic nature.) A presentation: 44% - 46% of urethane resin, 1 to 2% of triethylamine, 52 to 54% of water. pH: 7.8-8.8, ionicity: Anionic and coat characteristic:100% modulus 27 kgf/cm<sup>2</sup>, softening temperature of 80-90 \*\*. Dainippon Ink & Chemicals stock meeting incorporated company make;

H: Aquosity polyether polyether system urethane resin "binder CB-556" (a presentation: 35% - 45% of polyether polyether system urethane resin) Polyethylene-glycol mono- (or JI) fatty-acid (8-38) ester (n> 100), pH:alkalescence, ionicity:anionic, a coat: Elasticity, a water resisting property, and solvent resistance are excellent. What diluted wood chemical industry incorporated company make with ion exchange water twice;

I: Acrylic resin emulsion "VONCOAT OC-119H" (39% of a nonvolatile matter, the viscosity 1000 - 5000 mPa-s, particle electrification: an anion, coat characteristic:Tg10 \*\*, 100% modulus 7.9MPa, tensile strength 18MPa, Dainippon Ink and Chemicals Inc. make);

J: a carboxyl group content polyethylene-system-resin emulsion -- "the better -- sol --" (soap free colloid emulsion which used ethylene acrylic acid copolymer resin as the main ingredients, and blended the cross linking agent and the various-physical-properties grant agent.) Translucent sol-like liquid. A water-insoluble sex skin film with the structure of cross linkage is formed after 20% of solid content, 500 or less cP of viscosity, pH seven to 11 liquid density 1.0-1.1, the particle diameter of 0.07 micrometer, and moisture evaporation. The coating hardness 2H, Seishin Enterprise Make;

K: an aquosity fluoro-resin "die ERURA textile GLS-213CR" (a presentation -- : -- 20 to 30% of fluorocarbon rubber, 20 to 30% of fluoro-resin, and polyoxyethylene octylphenyl ether 2.2%, 40 to 50% of water, pH:8-10, and curing temperature:120-350 \*\*)

Viscosity: Excel in 50 - 130 mPa-s, coat:non cohesiveness, and lubricity. DAIKIN INDUSTRIES LTD. make

[0025]

[Working example 1]

100 copies of E-1, 0.5 copy of F-1, and two copies of F-2 were added to 100 copies of A-1, the T.K. homomixer MARKII2.5 type (made by special opportunity-ized industrial incorporated company) was used, agitation mixing was carried out for 5 minutes at 5,000 rpm, and the aquosity emulsion was prepared.

next, this aquosity emulsion -- the compounding ratio of Table 1 -- B, C, and D -- each was added, stirring mixing was carried out and it degassed with the vacuum pump. Next, each degassed sample was slushed into the 2-mm-thick sheet-shaped metallic mold, under application of pressure, apply for 10 minutes and it was made to harden, and the obtained silicone rubber sponge Mr. sheet was put into 150 \*\* hot wind circle method oven, hot air drying was carried out over 1 hour, and 90 \*\* of sheet shaped silicone sponge rubbers were obtained. This silicone sponge rubber was pierced with the No. 3 dumbbell, the piece of a dumbbell was immersed in each aqueous resin G, H, and I, J, and K, the situation of HAJIKI was observed, and that result was shown in Table 1. This result showed that the silicone sponge rubber Plastic solid by this invention did not have HAJIKI of aqueous resin, and resin membrane could be formed uniformly.

[0026]

[Working example 2]

50 copies of E-1, 50 copies of E-2, 0.5 copy of F-1, and two copies of F-2 were added to 100 copies of A-1, and the aquosity silicone emulsion was prepared on the same conditions as the working example 1. next, this aquosity silicone emulsion -- the compounding ratio of Table 1 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced in the same procedure as the working example 1. HAJIKI was observed by the same method as the working example 1, and the result was shown in Table 1.

[0027]

## [Comparative example 1]

100 copies of E-3 and five copies of F-3 were added to 100 copies of A-1, and the aqueous silicone emulsion was prepared on the same conditions as the working example 1. next, the compounding ratio of Table 1 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced in the same procedure as the working example 1. HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell of the uneven cell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0028]

## [Comparative example 2]

100 copies of E-3, 0.5 copy of F-1, and two copies of F-2 were added to 100 copies of A-1, and the emulsion was produced in the same procedure as the working example 1, next the silicone sponge rubber sheet was produced in the same procedure as the working example 1, HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0029]

## [Comparative example 3]

50 copies of E-3 and 1.0 copy of F-1 were added to 100 copies of A-1, and the emulsion was produced in the same procedure as the working example 1, next the silicone sponge rubber sheet of the uneven cell was produced in the same procedure as the working example 1, HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0030]

## [The comparative example 4]

50 copies of E-4 and 5.0 copies of F-1 were added to 100 copies of A-1, and an emulsion was produced in the same procedure as an working example 1, next a silicone sponge rubber sheet was produced in the same procedure as an working example 1, HAJIKI to aqueous resin was investigated by a piece of the No. 3 dumbbell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0031]

## [An working example 3]

An aqueous silicone emulsion was prepared on the same conditions as an working example 1. Next, with a compounding ratio of Table 2, B, C, and D were added, respectively, stirring mixing was carried out, and sheet shaped silicone sponge rubber was produced in the same procedure as an working example 1. After piercing this silicone sponge rubber with the No. 3 dumbbell and making it immersed in G, it put into 110 °C hot wind type oven for 10 minutes, it dried over 20 hours at a room temperature after that, and resin membrane which has the film pressure shown in the uniform table 2 was made to form. Tensile strength and a wear rate of silicone sponge rubber which have this resin membrane were measured, and it was shown in Table 2. This result shows that silicone sponge rubber which has the uniform resin membrane by this invention has high mechanical strength and abrasion resistance.

[0032]

## [An working example 4]

50 copies of E-1, 50 copies of E-2, and 0.5 copy of F-1 were added to 100 copies of A-1, and an aqueous silicone emulsion was prepared on the same conditions as an working example 1. next, this emulsion -- a compounding ratio of Table 2 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced in the same procedure as an working example 1. This silicone sponge rubber was pierced with the No. 3 dumbbell, and it was immersed in H, it dried by the same drying condition as an working example 3, and resin membrane which has the thickness shown in the uniform table 2 was made to form. Tensile strength and a wear rate of silicone sponge rubber which have this resin membrane were measured, and it was

shown in Table 2.

[0033]

[An working example 5]

100 copies of E-2, 2.0 copies of F-4, and 2.0 copies of F-5 were added to 100 copies of A-2, and an aqueous silicone emulsion was prepared on the same conditions as an working example 1. next, this emulsion -- a compounding ratio of Table 2 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced on the same conditions as an working example 1. This silicone sponge rubber was pierced with the No. 3 dumbbell, and it was immersed in H, it dried by the same drying condition as an working example 3, and resin membrane which has the thickness shown in the uniform table 2 was made to form. Tensile strength and a wear rate of silicone sponge rubber which have this resin membrane were measured, and it was shown in Table 2.

[0034]

[The comparative example 5]

Density of sheet shaped silicone sponge rubber (it does not have a coat of aqueous resin) produced in working example 3, hardness, tensile strength, and a wear rate were measured, and it was shown in Table 3.

[0035]

[The comparative example 6]

Density of sheet-shaped silicone sponge rubber (it does not have a coat of aqueous resin) produced in working example 4, hardness, tensile strength, and a wear rate were measured, and it was shown in Table 3.

[0036]

[The comparative example 7]

Density of sheet-shaped silicone sponge rubber (it does not have a coat of aqueous resin) produced in working example 5, hardness, tensile strength, and a wear rate were measured, and it was shown in Table 3.

[0037]

[Table 1]

## 水性樹脂のハジキ

	実施例1	実施例2	比較例1	比較例2	比較例3	比較例4
A-1	100	100	100	100	100	100
B	0.5	1.5	1.5	1.5	1.5	1.5
C	0.3	0.3	0.3	0.3	0.3	0.3
D	0.01	0.01	0.01	0.01	0.01	0.01
E-1	100	50				
E-2		50				
E-3			100	100	50	
E-4						50
F-1	0.5	0.5		0.5	1.0	5
F-2	2.0	2.0		2.0		
F-3			5			
G	無し	無し	有り	有り	有り	有り
H	無し	無し	有り	有り	有り	有り
I	無し	無し	有り	有り	有り	有り
J	無し	無し	有り	有り	有り	有り
K	無し	無し	有り	有り	有り	有り

[0038]

[Table 2]

水性樹脂皮膜の特性

	実施例3	実施例4	実施例5
A-1	100	100	
A-2			100
B	1.5	1.5	1.0
C	0.3	0.3	0.3
D	0.01	0.01	0.01
E-1	100	50	
E-2		50	100
F-1	0.5	0.5	
F-2	2.0		
F-4			2.0
F-5			2.0
G膜厚(μm)	50		
H膜厚(μm)		20	20
密度(g/cm <sup>3</sup> )	—	—	—
硬さ	—	—	—
引張強さ(MPa)	0.32	0.29	0.12
摩耗率(%)	7.0	3.7	13.1

[0039]

[Table 3]

## 水性樹脂皮膜の特性

	比較例5	比較例6	比較例7
A-1	100	100	
A-2			100
B	1.5	1.5	1.0
C	0.3	0.3	0.3
D	0.01	0.01	0.01
E-1	100	50	
E-2		50	100
F-1	0.5	0.5	
F-2	2.0		
F-4			2.0
F-5			2.0
G膜厚(μm)	—	—	—
H膜厚(μm)	—	—	—
密度(g/cm <sup>3</sup> )	0.61	0.60	0.60
硬さ	14	30	18
引張強さ(MPa)	0.15	0.24	0.04
摩耗率(%)	15.4	34.8	40.3

[Industrial applicability]

[0040]

The silicone sponge rubber Plastic solid which has the resin membrane of this invention is useful as the coating membrane of textiles or a nonwoven fabric, the coating membrane of glass crossing, an insulating sheet, a cushion, packing, a fixed form sealant, etc. The manufacturing method of the silicone sponge rubber Plastic solid which has the resin membrane of this invention is useful although the silicone sponge rubber Plastic solid which has resin membrane is manufactured with efficiency and sufficient productivity.

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TECHNICAL FIELD

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[Field of the Invention]

[0001]

This invention relates to an addition reaction hardening type silicone sponge rubber Plastic solid which has resin membrane, and a manufacturing method for the same.

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PRIOR ART

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[Background of the Invention]

[0002]

The outstanding buffer nature and vibration proof are evaluated and silicone sponge rubber is widely used for sporting gear, an INSHU letter, etc. Since various characteristics, such as pliability, elasticity, firmness, and feel nature, are provided, it may be used for the putt for ready figures which modeled form on the female udder the puff for makeup, and aimed at obtaining the ready figure. It excels in heat resistance and weatherability, and since it is lightweight, taking advantage of this characteristic, it is used as a surface coating material; structural fixed form sealant of part; copying machine rolls, such as packing, a gasket, and an O ring, etc. Conventionally, many constituents are proposed for [ this ] silicone rubber sponge formation as follows. For example, the silicone rubber sponge plasticity constituent which blends the pyrolysis type organic blowing agent represented by azobisisobutyronitrile is taught to JP,44-461,B and JP,7-247436,A.

A coat is thermoplastics and the silicone rubber sponge plasticity constituent which blends the balloon which included volatile hydrocarbon like butane or isobutane is proposed by JP,5-209080,A. In JP,54-135865,A and JP,5-70692,A. It consists of the water or alcohol, and the platinum system catalyst of alkenyl-group content diorganopolysiloxane, the ORGANO hydrogen polysiloxane, and a small quantity, The silicone rubber sponge plasticity constituent made to foam with the hydrogen gas emitted at the reaction of this ORGANO hydrogen polysiloxane and water is taught.

The emulsion which becomes JP,7-122000,B from organopolysiloxane, an emulsifier, water, and a viscous agent is contained as a foaming agent, The silicone rubber sponge plasticity constituent made to foam using evaporation of water and expansion is taught, and to JP,2002-114860,A.

Hydrosilylation reaction cross-linking which consists of alkenyl-group content diorganopolysiloxane, an ORGANO hydrogen polysiloxane, and a platinum system catalyst, That is, it is an addition reaction hardening setup-of-tooling product, and the silicone rubber sponge plasticity constituent containing the water-absorbent-polymer powder containing water is taught.

However, the problem of being hard to become is among the sponge which has a fine cell of what can form a complicated-shaped three-dimensional Plastic solid from these silicone rubber sponge plasticity constituent.

Then, this invention persons invented and did patent application about the method of manufacturing silicone rubber sponge, from the addition reaction hardening type aqueous silicone emulsion containing an emulsifier and water-soluble polymer (application for patent 2002-311470).

[0003]

However, the thing which has that possible the silicone sponge rubber produced from the emulsion for addition reaction hardening type silicone rubber sponge containing an emulsifier and water-soluble polymer forms a complicated-shaped three-dimensional Plastic solid, the mechanical strength of the acquired Plastic solid is low --- moreover --- the surface --- a scratch --- scratching --- etc. --- he has noticed that there is a problem of being easy to be damaged by a physical impact.

It is publicly known one (refer to JP,59-37580,A) to coat the surface of silicone rubber sponge with room-temperature-vulcanization type silicone rubber, and to protect this surface, Coating the surface of an emulsifier and the addition reaction hardening type silicone rubber sponge containing water-soluble polymer with room-temperature-vulcanization type silicone rubber is happening to think easily, if it is a person skilled in the art. However, in order to coat uniformly the surface of an emulsifier and the addition reaction hardening type silicone rubber sponge containing water-soluble polymer with room-temperature-vulcanization type silicone rubber, it is necessary to melt and coat organic solvents, such as toluene, with room-temperature-vulcanization type silicone rubber, and is not desirable on safety and hygiene. even if it can coat -- a scratch -- scratching -- etc. -- it is insufficient for protecting from damage by a physical impact.

[0004]

[Patent documents 1] JP,S44-461,B

[Patent documents 2] JP,H7-247436,A

[Patent documents 3] JP,H5-209080,A

[Patent documents 4] JP,S54-135865,A

[Patent documents 5] JP,H5-70692,A

[Patent documents 6] JP,H7-122000,B

[Patent documents 7] JP,2002-114860,A

[Patent documents 8] JP,S59-37580,A

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**EFFECT OF THE INVENTION**

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[Effect of the Invention]

[0007]

The silicone sponge rubber Plastic solid which has the resin membrane of this invention, the resin membrane of aqueous resin -- excelling in a mechanical strength, since the hardening resin coat of aqueous hardening resin is preferably laminated by the surface of the silicone sponge rubber Plastic solid -- a scratch -- scratching -- etc. -- even if it receives a physical impact, it is hard to be damaged, namely, rubfastness is excellent.

According to the manufacturing method of the silicone sponge rubber Plastic solid which has the resin membrane of this invention, excelling in a mechanical strength -- a scratch -- scratching -- etc. -- it is hard to be damaged even if it receives a physical impact. The resin membrane of aqueous resin and the silicone sponge rubber Plastic solid in which the hardening resin coat of hardenability aqueous resin is preferably laminated by the surface of the silicone sponge rubber Plastic solid can be manufactured simply and efficiently.

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TECHNICAL PROBLEM

[Problem to be solved by the invention]

[0005]

then -- this invention persons compensate the shortage of a mechanical strength of an addition reaction hardening type silicone rubber sponge Plastic solid -- a scratch -- scratching -- etc. -- it inquired wholeheartedly that the addition reaction hardening type silicone rubber sponge Plastic solid protected from damage by a physical impact should be developed, and this invention was reached.

the purpose of this invention compensates the shortage of a mechanical strength of an addition reaction hardening type silicone rubber sponge Plastic solid -- a scratch -- scratching -- etc. -- providing the addition reaction hardening type silicone rubber sponge Plastic solid which is hard to damage even if it receives a physical impact. And it is in providing the manufacturing method of this addition reaction hardening type silicone rubber sponge Plastic solid.

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MEANS

[Means for solving problem]

[0006]

These purposes, "(1) A silicone sponge rubber Plastic solid which has resin membrane, wherein resin membrane of aqueous resin is laminated by addition reaction hardening type silicone sponge rubber Plastic solid surface containing an emulsifier and water-soluble polymer.

(2) A silicone sponge rubber Plastic solid which has the resin membrane given in (1) forming from an addition reaction hardening type aqueous silicone emulsion in which an addition reaction hardening type silicone sponge rubber Plastic solid contains an emulsifier and water-soluble polymer.

(3) A silicone sponge rubber Plastic solid which has the resin membrane given in (1) being what chosen from a group which aqueous resin becomes from aqueous urethane system resin, aqueous acrylic resin, and an aqueous fluoro-resin.

(4) (1) - (3), wherein aqueous resin is hardenability is a silicone sponge rubber Plastic solid of a description either.

(5) A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane applying aqueous resin to an addition reaction hardening type silicone sponge rubber Plastic solid surface containing an emulsifier and water-soluble polymer, drying this aqueous resin after an appropriate time, and forming resin membrane.

(6) A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane given in (5) forming from an addition reaction type aqueous silicone emulsion in which an addition reaction hardening type silicone sponge rubber Plastic solid contains an emulsifier and water-soluble polymer.

(7) A manufacturing method of a silicone sponge rubber Plastic solid which has the resin membrane given in (5) being what chosen from a group which aqueous resin becomes from aqueous urethane resin, an aqueous acrylic resin, and an aqueous fluoro-resin.

(8) either of (5) - (7), wherein aqueous resin is hardenability -- a manufacturing method of a silicone sponge rubber Plastic solid of a description. " -- it is attained.

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EXAMPLE

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[Working example]

[0022]

Hereafter, an working example and a comparative example of this invention are hung up. There is a weight section among an working example and a comparative example with a part, it is weight % which is with %, and viscosity shows a numerical value in 25 \*\*. This invention is not limited by these working examples.

[0023]

Each characteristic in an working example and a comparative example was measured on condition of the following.

Density of silicone sponge rubber: A silicone sponge rubber sheet was pierced to punch of a constant diameter, the weight and thickness of a sheet piece which were pierced were measured, and weight/volume ( $\text{g}/\text{cm}^3$ ) was computed as density.

HAJIKI of aqueous resin: HAJIKI when a piece of a dumbbell of silicone sponge rubber was immersed in aqueous resin and taken out was observed visually.

Hardness of silicone sponge rubber: According to JIS K6253, it measured using low-pressure load machine CL-150 (made by polymer meter incorporated company) for rubber hardness meters.

Tensile strength of silicone sponge rubber: It measured according to JIS K6251.

The wear rate of the silicone sponge rubber which has resin membrane: SUGA abrasion testing machine NUS-ISO-1 (made by Suga Test Instruments Co., Ltd.) was used, and it measured by the reciprocating-movement attrition test method. The roll kneader which stuck the abrasive paper of the particle size 1200 was rotated 30 times on the silicone sponge rubber sheet as 50g of loads. (Sample weight after front [ wear ] sample weight (mg)-wear (mg)) The sample weight before  $\times 100$  /wear was computed as a wear rate. The sample weight before wear was found by measuring the weight of the specimen which consists of the roll kneader touch area (30mmX15mm) and thickness (about 2 mm) of a silicone sponge rubber sheet.

[0024]

The ingredient used by the working example and the comparative example is as follows.

A-1: The chain both ends of viscosity 10,000 mPa-s 17 copies of hydrophobic fumed silica of specific surface area  $2[ \text{ of } 200 \text{ m } ]/\text{g}$  by which the surface treatment was carried out to 100 copies of dimethylpolysiloxane (0.14% of vinyl group content) blocked by the dimethylvinyl siloxy group by hexamethyldisilazane. Liquid liquid silicone rubber base which was mixed uniformly and prepared by performing heat treatment for 2 hours at 180 \*\*;

A-2: The viscosity 40, Aerosil R-972 which is the fumed silica by which the surface treatment was carried out to 100 copies of dimethylsiloxane methylvinyl siloxane copolymers (0.14% of vinyl group content) by which the chain both ends of 000 mPa-s were blocked with the trimethylsiloxy group by dimethyldichlorosilane. (Product made from Japanese Aerosil, Inc.) Liquid liquid silicone rubber base which mixed 17 copies uniformly and was prepared by performing heat treatment for 2 hours at 180

\*\*;

B: Both-ends trimethylsiloxy group blockade dimethylsiloxane methylhydrogensiloxane copolymer of viscosity 5 mPa·s (0.8% of silicon atom absorbed water matter content);

C: Complex of chloroplatinic acid and divinyl tetramethyl disiloxane;

D: All [ 3,5-dimethyl- 1-hexyne-3 ] as an addition reaction retardant;

E-1: Solution of sodium polyacrylate which is water-soluble polymer (1% of water-soluble polymer content);

E-2: Solution of the sodium salt of carboxymethyl cellulose which is water-soluble polymer (3% of water-soluble polymer content)

E-3: Water made to gel by the acrylate polymer partial sodium salt bridge construction thing which is a water-absorbent polymer (0.3% of water-absorbent-polymer content);

E-4: Ion exchange water

F-1: Polyoxyethylene dioleate (HLB value 10.4);

F-2: Polyoxyethylene dilaurate (HLB value 6.6);

F-3: Polyoxyethylene lauryl ether (HLB value 9.6);

F-4: Higher alcohol system non-ion system surface-active agent Selected Special Wax SS-50 (made by SANYO CHEMICAL INDUSTRIES LTD.) (HLB value 10.5);

F-5: Higher alcohol system non-ion system surface-active agent Selected Special Wax SS-70 (made by SANYO CHEMICAL INDUSTRIES LTD.) (HLB value 12.8);

G: Aquosity polyester system urethane resin "hide run HW-311" (it is aqueous urethane resin of a dissolution thru/or what is called colloidal dispersion type [ underwater ] extremely distributed in the shape of a particle in the urethane resin which has ionicity, i.e., the ion group whose urethane ionomer is the hydrophilic nature.) Presentation: 44% - 46% of urethane resin, 1 to 2% of triethylamine, 52 to 54% of water. pH: 7.8-8.8, ionicity: Anionic and coat characteristic: 100% modulus 27 kgf/cm<sup>2</sup>, softening temperature of 80-90 \*\*. Dainippon Ink & Chemicals stock meeting incorporated company make;

H: Aquosity polyether polyether system urethane resin "binder CB-556" (presentation: 35% - 45% of polyether polyether system urethane resin) Polyethylene-glycol mono- (or JI) fatty-acid (8-38) ester (n> 100), pH:alkalinescence, ionicity:anionic, a coat: Elasticity, a water resisting property, and solvent resistance are excellent. What diluted wood chemical industry incorporated company make with ion exchange water twice;

I: Acrylic resin emulsion "VONCOAT OC-119H" (39% of a nonvolatile matter, the viscosity 1000 - 5000 mPa·s, particle electrification: an anion, coat characteristic:Tg10 \*\*, 100% modulus 7.9MPa, tensile strength 18MPa, Dainippon Ink and Chemicals Inc. make);

J: a carboxyl group content polyethylene-system-resin emulsion -- "the better -- sol --" (soap free colloid emulsion which used ethylene acrylic acid copolymer resin as the main ingredients, and blended the cross linking agent and the various-physical-properties grant agent.) Translucent sol-like liquid. A water-insoluble sex skin film with the structure of cross linkage is formed after 20% of solid content, 500 or less cP of viscosity, pH seven to 11 liquid density 1.0-1.1, the particle diameter of 0.07 micrometer, and moisture evaporation. The coating hardness 2H, Seishin Enterprise Make;

K: an aquosity fluoro-resin "die ERURA textile GLS-213CR" (a presentation -- : -- 20 to 30% of fluorocarbon rubber, 20 to 30% of fluoro-resin, and polyoxyethylene octylphenyl ether 2.2%, 40 to 50% of water, pH:8-10, and curing temperature:120-350 \*\*)

Viscosity: Excel in 50 - 130 mPa·s, coat:non cohesiveness, and lubricity. DAIKIN INDUSTRIES LTD. make

[0025]

[Working example 1]

100 copies of E-1, 0.5 copy of F-1, and two copies of F-2 were added to 100 copies of A-1, the T.K. homomixer MARKII2.5 type (made by special opportunity-ized industrial incorporated company) was used, agitation mixing was carried out for 5 minutes at 5,000 rpm, and the aquosity emulsion



was prepared.

next, this aqueous emulsion -- the compounding ratio of Table 1 -- B, C, and D -- each was added, stirring mixing was carried out and it degassed with the vacuum pump. Next, each degassed sample was slushed into the 2-mm-thick sheet-shaped metallic mold, under application of pressure, apply for 10 minutes and it was made to harden, and the obtained silicone rubber sponge Mr. sheet was put into 150 °C hot wind circle method oven, hot air drying was carried out over 1 hour, and 90 °C of sheet shaped silicone sponge rubbers were obtained. This silicone sponge rubber was pierced with the No. 3 dumbbell, the piece of a dumbbell was immersed in each aqueous resin G, H, and I, J, and K, the situation of HAJIKI was observed, and that result was shown in Table 1. This result showed that the silicone sponge rubber Plastic solid by this invention did not have HAJIKI of aqueous resin, and resin membrane could be formed uniformly.

[0026]

[Working example 2]

50 copies of E-1, 50 copies of E-2, 0.5 copy of F-1, and two copies of F-2 were added to 100 copies of A-1, and the aqueous silicone emulsion was prepared on the same conditions as the working example 1. next, this aqueous silicone emulsion -- the compounding ratio of Table 1 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced in the same procedure as the working example 1. HAJIKI was observed by the same method as the working example 1, and the result was shown in Table 1.

[0027]

[Comparative example 1]

100 copies of E-3 and five copies of F-3 were added to 100 copies of A-1, and the aqueous silicone emulsion was prepared on the same conditions as the working example 1. next, the compounding ratio of Table 1 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced in the same procedure as the working example 1. HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell of the uneven cell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0028]

[Comparative example 2]

100 copies of E-3, 0.5 copy of F-1, and two copies of F-2 were added to 100 copies of A-1, and the emulsion was produced in the same procedure as the working example 1, next the silicone sponge rubber sheet was produced in the same procedure as the working example 1, HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0029]

[Comparative example 3]

50 copies of E-3 and 1.0 copy of F-1 were added to 100 copies of A-1, and the emulsion was produced in the same procedure as the working example 1, next the silicone sponge rubber sheet of the uneven cell was produced in the same procedure as the working example 1, HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0030]

[Comparative example 4]

50 copies of E-4 and 5.0 copies of F-1 were added to 100 copies of A-1, and the emulsion was produced in the same procedure as the working example 1, next the silicone sponge rubber sheet was produced in the same procedure as the working example 1, HAJIKI to aqueous resin was investigated by the piece of the No. 3 dumbbell, and it was shown in Table 1. Uniform resin membrane formation was difficult because of HAJIKI.

[0031]

[Working example 3]

The aqueosity silicone emulsion was prepared on the same conditions as the working example 1. Next, with the compounding ratio of Table 2, B, C, and D were added, respectively, stirring mixing was carried out, and sheet shaped silicone sponge rubber was produced in the same procedure as the working example 1. After piercing this silicone sponge rubber with the No. 3 dumbbell and making it immersed in G, it put into 110 °C hot wind type oven for 10 minutes, it dried over 20 hours at the room temperature after that, and the resin membrane which has the film pressure shown in the uniform table 2 was made to form. The tensile strength and the wear rate of silicone sponge rubber which have this resin membrane were measured, and it was shown in Table 2. This result shows that the silicone sponge rubber which has the uniform resin membrane by this invention has high mechanical strength and abrasion resistance.

[0032]

[An working example 4]

50 copies of E-1, 50 copies of E-2, and 0.5 copy of F-1 were added to 100 copies of A-1, and an aqueosity silicone emulsion was prepared on the same conditions as an working example 1. next, this emulsion -- a compounding ratio of Table 2 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced in the same procedure as an working example 1. This silicone sponge rubber was pierced with the No. 3 dumbbell, and it was immersed in H, it dried by the same drying condition as an working example 3, and resin membrane which has the thickness shown in the uniform table 2 was made to form. Tensile strength and a wear rate of silicone sponge rubber which have this resin membrane were measured, and it was shown in Table 2.

[0033]

[An working example 5]

100 copies of E-2, 2.0 copies of F-4, and 2.0 copies of F-5 were added to 100 copies of A-2, and an aqueosity silicone emulsion was prepared on the same conditions as an working example 1. next, this emulsion -- a compounding ratio of Table 2 -- B, C, and D -- each was added, stirring mixing was carried out and sheet shaped silicone sponge rubber was produced on the same conditions as an working example 1. This silicone sponge rubber was pierced with the No. 3 dumbbell, and it was immersed in H, it dried by the same drying condition as an working example 3, and resin membrane which has the thickness shown in the uniform table 2 was made to form. Tensile strength and a wear rate of silicone sponge rubber which have this resin membrane were measured, and it was shown in Table 2.

[0034]

[Comparative example 5]

The density of the sheet shaped silicone sponge rubber (it does not have a coat of aqueous resin) produced in working example 3, hardness, tensile strength, and a wear rate were measured, and it was shown in Table 3.

[0035]

[Comparative example 6]

The density of the sheet-shaped silicone sponge rubber (it does not have a coat of aqueous resin) produced in working example 4, hardness, tensile strength, and a wear rate were measured, and it was shown in Table 3.

[0036]

[Comparative example 7]

The density of the sheet-shaped silicone sponge rubber (it does not have a coat of aqueous resin) produced in working example 5, hardness, tensile strength, and a wear rate were measured, and it was shown in Table 3.

[0037]

[Table 1]

## 水性樹脂のハジキ

	実施例1	実施例2	比較例1	比較例2	比較例3	比較例4
A-1	100	100	100	100	100	100
B	0.5	1.5	1.5	1.5	1.5	1.5
C	0.3	0.3	0.3	0.3	0.3	0.3
D	0.01	0.01	0.01	0.01	0.01	0.01
E-1	100	50				
E-2		50				
E-3			100	100	50	
E-4						50
F-1	0.5	0.5		0.5	1.0	5
F-2	2.0	2.0		2.0		
F-3			5			
G	無し	無し	有り	有り	有り	有り
H	無し	無し	有り	有り	有り	有り
I	無し	無し	有り	有り	有り	有り
J	無し	無し	有り	有り	有り	有り
K	無し	無し	有り	有り	有り	有り

[0038]

[Table 2]

水性樹脂皮膜の特性

	実施例3	実施例4	実施例5
A-1	100	100	
A-2			100
B	1.5	1.5	1.0
C	0.3	0.3	0.3
D	0.01	0.01	0.01
E-1	100	50	
E-2		50	100
F-1	0.5	0.5	
F-2	2.0		
F-4			2.0
F-5			2.0
G膜厚( $\mu\text{m}$ )	50		
H膜厚( $\mu\text{m}$ )		20	20
密度( $\text{g}/\text{cm}^3$ )	—	—	—
硬さ	—	—	—
引張強さ(MPa)	0.32	0.29	0.12
摩耗率(%)	7.0	3.7	13.1

[0039]

[Table 3]

水性樹脂皮膜の特性

	比較例5	比較例6	比較例7
A-1	100	100	
A-2			100
B	1.5	1.5	1.0
C	0.3	0.3	0.3
D	0.01	0.01	0.01
E-1	100	50	
E-2		50	100
F-1	0.5	0.5	
F-2	2.0		
F-4			2.0
F-5			2.0
G膜厚(μm)	—	—	—
H膜厚(μm)	—	—	—
密度(g/cm <sup>3</sup> )	0.61	0.60	0.60
硬さ	14	30	18
引張強さ(MPa)	0.15	0.24	0.04
摩耗率(%)	15.4	34.8	40.3

[Translation done.]

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最終頁に続く

(54) 【発明の名称】 樹脂皮膜を有する付加反応硬化型シリコンスポンジゴム成形体およびその製造方法

## (57) 【要約】

【課題】強度と耐摩耗性に優れた樹脂皮膜を有するシリコンスポンジゴム成形体と、その製造方法を提供する。

【解決手段】乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体の表層に水性樹脂の樹脂皮膜が積層されている、樹脂皮膜を有するシリコンスポンジゴム成形体。

乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体表層に水性樹脂を塗布し、しかる後該水性樹脂を乾燥して樹脂皮膜を形成する、樹脂皮膜を有するシリコンスポンジゴム成形体の製造方法。

【選択図】なし

## 【特許請求の範囲】

## 【請求項1】

乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンスポンジゴム成形体の表層に水性樹脂の樹脂皮膜が積層されていることを特徴とする樹脂皮膜を有するシリコーンスポンジゴム成形体。

## 【請求項2】

付加反応硬化型シリコーンスポンジゴム成形体が乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルジョンから形成されたものであることを特徴とする請求項1記載の樹脂皮膜を有するシリコーンスポンジゴム成形体。

## 【請求項3】

水性樹脂が水性ウレタン系樹脂、水性アクリル系樹脂および水性フッ素樹脂からなる群から選択されるものであることを特徴とする請求項1記載の樹脂皮膜を有するシリコーンスポンジゴム成形体。

## 【請求項4】

水性樹脂が硬化性であることを特徴とする請求項1～請求項3のいずれか1項記載のシリコーンスポンジゴム成形体。

## 【請求項5】

乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンスポンジゴム成形体表層に水性樹脂を塗布し、しかる後該水性樹脂を乾燥して樹脂皮膜を形成することを特徴とする樹脂皮膜を有するシリコーンスポンジゴム成形体の製造方法。

## 【請求項6】

付加反応硬化型シリコーンスポンジゴム成形体が乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルジョンから形成されたものであることを特徴とする請求項5記載の樹脂皮膜を有するシリコーンスポンジゴム成形体の製造方法。

## 【請求項7】

水性樹脂が水性ウレタン樹脂、水性アクリル樹脂または水性フッ素樹脂から選択されるものであることを特徴とする請求項5記載の樹脂皮膜を有するシリコーンスポンジゴム成形体の製造方法。

## 【請求項8】

水性樹脂が硬化性であることを特徴とする請求項5～請求項7のいずれか1項記載のシリコーンスポンジゴム成形体の製造方法。

## 【発明の詳細な説明】

## 【技術分野】

## 【0001】

本発明は樹脂皮膜を有する付加反応硬化型シリコーンスポンジゴム成形体およびその製造方法に関する。

## 【背景技術】

## 【0002】

シリコーンスポンジゴムは優れた緩衝性や防振性が評価され、スポーツ用具やインシュレーターなどに広く利用されている。また、柔軟性、弾力性、保形性、感触性などの諸特性を具備しているために、化粧用パフや整姿目的で女性の乳房に形状を似せた整姿用パットに使用されることがある。また、耐熱性、耐候性に優れ、軽量であることから、かかる特性を活かして、パッキング、ガスケット、Oリング等の部品；複写機ロールの表面被覆材；建築用定形シール材などとして使用されている。従来、かかるシリコーンゴムスポンジ形成用に、以下のとおり数多くの組成物が提案されている。例えば、特公昭44-461と特開平7-247436には、アゾビスイソブチロニトリルに代表される熱分解型有機発泡剤を配合してなるシリコーンゴムスポンジ形成性組成物が教示されており、特開平5-209080には、外殻が熱可塑性プラスチックであり、ブタンやイソブタンのような揮発性炭化水素を内包したバルーンを配合してなるシリコーンゴムスポンジ形成性組成物が提案されている。特開昭54-135865と特開平5-70692には、アルケニル基

含有ジオルガノポリシロキサンとオルガノハイドロジェンポリシロキサンと少量の水もしくはアルコールと白金系触媒とからなり、該オルガノハイドロジェンポリシロキサンと水との反応で発生した水素ガスによって発泡させるシリコーンゴムスポンジ形成性組成物が教示されており、特公平7-122000には、オルガノポリシロキサン、乳化剤、水および粘調剤からなるエマルジョンを発泡剤として含有し、水の蒸発、膨張を利用して発泡させるシリコーンゴムスポンジ形成性組成物が教示されており、特開2002-114860には、アルケニル基含有ジオルガノポリシロキサン、オルガノハイドロジェンポリシロキサンおよび白金系触媒からなるヒドロシリル化反応架橋性、すなわち、付加反応硬化型組成物であって、水を含有した吸水性ポリマー粉末を含有するシリコーンゴムスポンジ形成性組成物が教示されている。ところが、これらシリコーンゴムスポンジ形成性組成物から複雑な形状の立体的成形体を形成することはできるものの、細かいセルを有するスポンジにはなりにくいという問題がある。

そこで、本発明者らは、乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルジョンからシリコーンゴムスポンジを製造する方法について発明をして特許出願した(特願2002-311470)。

#### 【0003】

ところが、乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンゴムスポンジ用エマルジョンから作製されるシリコーンスポンジゴムは複雑な形状の立体的成形体を形成することは可能なものの、得られた成形体の機械的強度は低く、しかも、その表層は擦過や引掻きなどの物理的衝撃によって損傷し易いという問題があることに気づいた。シリコーンゴムスポンジの表面に室温加硫型シリコーンゴムをコーティングして該表面を保護することは公知である(特開昭59-37580参照)ので、乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンゴムスポンジの表面を室温加硫型シリコーンゴムでコーティングすることは当業者であれば容易に思いつくことである。ところが、乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンゴムスポンジの表面を室温加硫型シリコーンゴムで均一にコーティングするには、室温加硫型シリコーンゴムをトルエン等の有機溶剤に溶かしてコーティングする必要がある、安全衛生上好ましくない。仮にコーティングできても擦過や引掻きなどの物理的衝撃による損傷から保護するには不十分である。

#### 【0004】

【特許文献1】特公昭44-461号公報

【特許文献2】特開平7-247436号公報

【特許文献3】特開平5-209080号公報

【特許文献4】特開昭54-135865号公報

【特許文献5】特開平5-70692号公報

【特許文献6】特公平7-122000号公報

【特許文献7】特開2002-114860号公報

【特許文献8】特開昭59-37580号公報

【発明の開示】

【発明が解決しようとする課題】

#### 【0005】

そこで、本発明者らは、付加反応硬化型シリコーンゴムスポンジ成形体の機械的強度不足を補い、擦過や引掻きなどの物理的衝撃による損傷から保護される付加反応硬化型シリコーンゴムスポンジ成形体を開発すべく鋭意検討して本発明に到達した。

本発明の目的は、付加反応硬化型シリコーンゴムスポンジ成形体の機械的強度不足を補い、擦過や引掻きなどの物理的衝撃を受けても損傷しにくい付加反応硬化型シリコーンゴムスポンジ成形体を提供すること、および、かかる付加反応硬化型シリコーンゴムスポンジ成形体の製造方法を提供することにある。

【課題を解決するための手段】

#### 【0006】

これら目的は、「(1) 乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンス



ポンジゴム成形体表層に水性樹脂の樹脂皮膜が積層されていることを特徴とする樹脂皮膜を有するシリコンスポンジゴム成形体。

(2) 付加反応硬化型シリコンスポンジゴム成形体が乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコンエマルジョンから形成されたものであることを特徴とする(1)記載の樹脂皮膜を有するシリコンスポンジゴム成形体。

(3) 水性樹脂が水性ウレタン系樹脂、水性アクリル系樹脂および水性フッ素樹脂からなる群から選択されるものであることを特徴とする(1)記載の樹脂皮膜を有するシリコンスポンジゴム成形体。

(4) 水性樹脂が硬化性であることを特徴とする(1)～(3)のいずれか記載のシリコンスポンジゴム成形体。

(5) 乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体表層に水性樹脂を塗布し、しかる後該水性樹脂を乾燥して樹脂皮膜を形成することを特徴とする樹脂皮膜を有するシリコンスポンジゴム成形体の製造方法。

(6) 付加反応硬化型シリコンスポンジゴム成形体が乳化剤と水溶性ポリマーを含有する付加反応型水性シリコンエマルジョンから形成されたものであることを特徴とする(5)記載の樹脂皮膜を有するシリコンスポンジゴム成形体の製造方法。

(7) 水性樹脂が水性ウレタン樹脂、水性アクリル樹脂および水性フッ素樹脂からなる群から選択されるものであることを特徴とする(5)記載の樹脂皮膜を有するシリコンスポンジゴム成形体の製造方法。

(8) 水性樹脂が硬化性であることを特徴とする(5)～(7)のいずれか記載のシリコンスポンジゴム成形体の製造方法。」により達成される。

#### 【発明の効果】

##### 【0007】

本発明の樹脂皮膜を有するシリコンスポンジゴム成形体は、水性樹脂の樹脂皮膜、好ましくは水性硬化性樹脂の硬化樹脂皮膜がシリコンスポンジゴム成形体の表層に積層されているので、機械的強度に優れ、擦過や引掻きなどの物理的衝撃を受けても損傷しにくい、すなわち、耐擦過性が優れている。

本発明の樹脂皮膜を有するシリコンスポンジゴム成形体の製造方法によると、機械的強度に優れ、擦過や引掻きなどの物理的衝撃を受けても損傷しにくい、水性樹脂の樹脂皮膜、好ましくは硬化性水性樹脂の硬化樹脂皮膜がシリコンスポンジゴム成形体の表層に積層されているシリコンスポンジゴム成形体を簡易に、かつ、効率的に製造することができる。

#### 【発明を実施するための最良の形態】

##### 【0008】

本発明における樹脂皮膜を有するシリコンスポンジゴム成形体は、乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体の表層に水性樹脂の樹脂皮膜が積層されており、該樹脂皮膜は付加反応硬化型シリコンスポンジゴム成形体の表層を被覆し付加反応硬化型シリコンスポンジゴム成形体によく密着ないし接着している。乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体は、シート状、ブロック状、角柱状、丸棒状、球状など、用途に応じて適宜必要な形状と大きさを取ることができる。他の基材、例えば織物、不織布、硝子クロス、金属板、合板上のコーティング膜であってもよい。その密度はスポンジゴムが通常有する密度でよく、0.2～0.9、好ましくは0.4～0.7である。内在するセルの径は、乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体の製造方法によって変わってくるので、一概に規定できないが、下記の乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコンエマルジョンを硬化させ、ついで加熱して乾燥することにより、あるいは加熱して硬化させつつ脱水することにより製造された場合は、例えば0.05～0.2mmである。もちろん、0.1～0.3mm、0.2～0.5mmなど種々の大きさと分布をとることができる。乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコンスポンジゴム成形体は、水性樹脂の樹脂皮膜の密着性ないし接着性の観点から、好まし

くは乳化剤を0.01~10重量%、水溶性ポリマーを0.01~15重量%含有し、加熱時の黄変防止の観点から好ましくは乳化剤を0.01~3重量%、水溶性ポリマーを0.01~2.5重量%含有するとよい。

【0009】

乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンスポンジゴム成形体の製造方法は、特に限定されず、例えば、乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルジョンを硬化させ、ついで加熱して乾燥することにより、あるいは加熱して硬化させつつ脱水することにより製造することができる。

乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルジョンは、成分上は、少なくとも(A)1分子中に少なくとも2個のアルケニル基を有するジオルガノポリシロキサン、(B)ケイ素原子結合水素を有するオルガノポリシロキサン、(C)白金系触媒、(D)乳化剤、(E)水溶性ポリマーおよび(F)水からなるが、(A)1分子中に少なくとも2個のアルケニル基を有するジオルガノポリシロキサン、(B)ケイ素原子結合水素を有するオルガノポリシロキサンおよび(D)白金系触媒からなる付加反応硬化型液状シリコーンゴム組成物を(D)乳化剤により(E)水溶性ポリマーの水溶液に乳化することにより、あるいは、(A)1分子中に少なくとも2個のアルケニル基を有するジオルガノポリシロキサンを(D)乳化剤により(F)水溶性ポリマーの水溶液に乳化し、ついで、(B)ケイ素原子結合水素を有するオルガノポリシロキサンおよび(C)白金系触媒を添加し混合することにより製造することができる。

【0010】

ここで、(A)1分子中に少なくとも2個のケイ素原子結合アルケニル基を有するジオルガノポリシロキサンは、主剤であり、該アルケニル基がケイ素原子結合水素を有するオルガノポリシロキサンの該水素原子と付加反応して架橋し、硬化する。

アルケニル基としてはビニル基、アリル基、プロペニル基が例示される。アルケニル基以外の有機基としては、メチル基、エチル基、プロピル基などのアルキル基；フェニル基、トリル基などのアリール基；3,3,3-トリフロロプロピル基、3-クロロプロピル基などのハロアルキル基が例示されるが、メチル基が好ましい。本成分の分子構造は直鎖状が好ましく、軽度に分枝した鎖状であってもよい。本成分の分子量は特に限定されないが、25℃における粘度が100mPa・s以上、100,000mPa・s以下であることが好ましい。上記ジオルガノポリシロキサンは、2種以上を併用してもよい。

【0011】

(B)1分子中に少なくとも2個のケイ素原子結合水素原子を有するオルガノポリシロキサンは、白金系触媒の存在下にそのケイ素原子結合水素原子が、ジオルガノポリシロキサン(A)のケイ素原子結合アルケニル基に付加反応して架橋、硬化させるものである。したがって、ジオルガノポリシロキサン(A)がアルケニル基を2個有するときは、本成分は1分子中に3個以上のケイ素原子結合水素原子を有することが必要である。ケイ素原子結合有機基としては、メチル基、エチル基、プロピル基などのアルキル基；フェニル基、トリル基などのアリール基；3,3,3-トリフロロプロピル基、3-クロロプロピル基などのハロゲン化アルキル基が例示されるが、メチル基が好ましい。本成分の分子構造は、直鎖状、分枝状、環状、網目状などのいずれでもよい。本成分の分子量は特に限定されないが、25℃における粘度が1mPa・s以上、10,000mPa・s以下であることが好ましい。オルガノポリシロキサン(B)中のケイ素原子結合水素原子とジオルガノポリシロキサン(A)中のケイ素原子結合アルケニル基のモル比は、両者が架橋し硬化してゴム状を呈する範囲であれば特に限定されないが、通常、0.5~3くらいである。

【0012】

(C)白金系触媒は、オルガノポリシロキサン(B)中のケイ素原子結合水素原子のジオルガノポリシロキサン(A)中のケイ素原子結合アルケニル基への付加反応を促進する触媒であり、白金微粉末、白金黒、塩化白金酸、塩化白金酸のオレフィン錯体、塩化白金酸のアルケニルシロキサンとの錯化合物、ロジウム化合物、パラジウム化合物が例示される。その使用量は、オルガノポリシロキサン(B)中のケイ素原子結合水素原子のジオルガ

ノポリシロキサン (A) 中のケイ素原子結合アルケニル基への付加反応を促進して、架橋、硬化させるのに十分な量、いわゆる触媒量である。

【0013】

(D) 乳化剤は、(A) 1分子中に少なくとも2個のケイ素原子結合アルケニル基を有するジオルガノポリシロキサン、(B) 1分子中に少なくとも2個のケイ素原子結合水素原子を有するオルガノポリシロキサン、あるいは、(A) 1分子中に少なくとも2個のアルケニル基を有するジオルガノポリシロキサン、(B) ケイ素原子結合水素を有するオルガノポリシロキサンおよび(C) 白金系触媒からなる付加反応硬化型液状シリコンゴム組成物を水中に乳化して安定なエマルジョンを形成するために配合される。乳化能にすぐれ、付加反応を阻害しなければ、その種類は特に限定されないが、一般に非イオン系の乳化剤が好ましい。非イオン系の乳化剤としての非イオン系界面活性剤は、ポリオキシエチレンアルキルエーテル、ポリオキシエチレンフェニールエーテル、エチレングリコールモノ脂肪酸エステル、プロピレングリコールモノ脂肪酸エステル、ソルビタンモノ脂肪酸エステル、ソルビタントリ脂肪酸エステル、ポリオキシエチレンモノ脂肪酸エステル、ポリオキシエチレンジ脂肪酸エステル、ポリオキシエチレンプロピレングリコール脂肪酸エステルあるいはPOE多価アルコール類が例示される。乳化剤のHLB値は4~14のものが好ましい。乳化剤は2種以上を併用してもよい。乳化剤の配合量は、ジオルガノポリシロキサン(A) 100重量部に対して好ましくは0.1~15重量部、より好ましくは0.5~12重量部である。0.1重量部より少ないと安定なシリコンエマルジョンとはなり難く、15重量部を超えると硬化して得られるシリコンスポンジゴムの物理特性が低下しがちであるからである。

【0014】

(E) 水溶性ポリマーは、水性シリコンエマルジョンを調製する際に(D) 乳化剤の減量に効果があるとともに、水溶性ポリマーと乳化剤の併用は、シリコンスポンジゴム成形体に水性樹脂を塗布した際のハジキ低減に著しい効果がある。水溶性ポリマーとしてはアルギン酸、アルギン酸ナトリウム、カラギーナン；カルボキシメチルセルロースのナトリウム塩；メチルセルロース、エチルセルロース、ヒドロキシエチルセルロース等のセルロースエーテル；変性デンプン、ポリビニールアルコール、ポリアクリル酸ナトリウム塩、ポリメタアクリル酸ナトリウム塩が例示される。(E) 水溶性ポリマーの種類によって異なるが、水溶液中の含有量は、好ましくは0.1~5重量%、より好ましくは0.5~3重量%である。その量が0.1重量%より少ないときは水性ポリマー水溶液の粘性が低くて安定なエマルジョンが得難く、5重量%を超えるとときは粘性が高過ぎて攪拌が困難となることがあるからである。

【0015】

(F) 水は、上記成分(A)と成分(B)と成分(C)、あるいは成分(A)~成分(C)からなる付加反応硬化型液状シリコンゴム組成物を乳化させる媒体であり、清浄であればよく、その種類は制限されない。水道水、井戸水、イオン交換水、蒸留水が例示される。水の使用量は、上記成分(A)と成分(B)と成分(C)、あるいは成分(A)~成分(C)からなる付加反応硬化型液状シリコンゴム組成物を乳化させ、硬化時にシリコンスポンジゴムの形成するのに十分な量であれば特に制限されないが、ジオルガノポリシロキサン(A) 100重量部当り好ましくは30~300重量部であり、より好ましくは50~200重量部である。30重量部より少ないと水性エマルジョンの形態をとり難く、300重量部を超えると形成されるシリコンスポンジゴムの強度が損なわれることがあるからである。

【0016】

この付加反応硬化型水性シリコンエマルジョンには、流動性を調節したり、硬化物の機械強度を向上させるために各種の充填剤を配合してもよく、このような充填剤としては、沈降シリカ、ヒュームドシリカ、カーボンブラック、焼成シリカ、コロイド状炭酸カルシウム、ヒュームド二酸化チタンなどの補強性充填剤；石英粉末、珪藻土、アルミノケイ酸、酸化マグネシウム、重質炭酸カルシウムなどの非補強性充填剤；これらのシリカ充填剤

をジメチルジクロロシラン、ヘキサメチルジシラザン、オクタメチルシクロテトラシロキサンなどの有機ケイ素化合物で疎水化処理したものが例示される。さらに、常温での硬化を抑制するために、付加反応抑制剤を配合することが好ましい。さらに、必要に応じてアルコール類、顔料、耐熱剤、難燃剤、可塑剤、接着付与剤などを配合してもよい。

【0017】

少なくとも(A)1分子中に少なくとも2個のアルケニル基を有するジオルガノポリシロキサン、(B)ケイ素原子結合水素を有するオルガノポリシロキサン、(C)白金系触媒、(D)乳化剤、(E)水溶性ポリマーおよび(F)水からなる付加反応硬化型水性シリコーンエマルションは、例えば次のような方法で製造することができる。

(1)所定量のアルケニル基を有するジオルガノポリシロキサン(A)、所定量のケイ素原子結合水素を有するオルガノポリシロキサン(B)、所定量の白金系触媒(C)、所定量の水溶性ポリマー(E)の水溶液と所定量の乳化剤(D)を高速攪拌ミキサーに投入し、所定時間攪拌混合する方法、

(2)所定量のアルケニル基を有するジオルガノポリシロキサン(A)と所定量のケイ素原子結合水素を有するオルガノポリシロキサン(B)と所定量の白金系触媒からなる付加反応硬化型液状シリコーンゴム組成物と所定量の水溶性ポリマー(E)の水溶液と所定量の乳化剤(D)を高速攪拌ミキサーに投入し、所定時間攪拌混合する方法、

(3)所定量のアルケニル基を有するジオルガノポリシロキサン(A)、所定量の水溶性ポリマー(E)の水溶液、所定量の乳化剤(D)を高速攪拌ミキサーに投入し、所定時間攪拌混合した後に、所定量のケイ素原子結合水素を有するオルガノポリシロキサン(B)と所定量の白金系触媒(C)を攪拌混合する方法。

なお、上記製造方法において、アルケニル基を有するジオルガノポリシロキサン(A)は常温で液状であり、あらかじめ補強性シリカフィラーと加熱下混合して調製されたペースト状物である液状シリコーンゴムベースの形で使用することが好ましい。

ここで使用するミキサーとしてはホモミキサー、パドルミキサー、ヘンシェルミキサー、ホモディスパー、コロイドミル、真空混合攪拌ミキサー等が例示されるが、安定なエマルションが得られるものであれば、特に限定されない。

【0018】

かかる乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルションが、攪拌混合時に気泡を巻き込んでいるときは、まず脱気することが好ましい。通常、脱気はミキサー内で攪拌中、または容器内に静置した状態で真空ポンプ等を使用しで減圧下で実施されるが、減圧度や脱気時間は特に限定されるものではなく、目視で気泡の存在のない範囲まで脱気操作を続ければよい。ついで、乳化剤と水溶性ポリマーを含有する付加反応硬化型水性シリコーンエマルションを、例えば、常温から150℃、好ましくは50℃から120℃の温度で硬化させるか、硬化しつつ脱水して、シリコーンスポンジゴム様成形体を形成する。ついで、このシリコーンスポンジゴム様成形体を100℃～250℃で乾燥すると水が除去されてシリコーンスポンジゴム成形体が形成される。シリコーンスポンジゴム様成形体は加熱乾燥時に黄変することがあるので、水洗してから加熱乾燥することが好ましい。

その成形方法は圧縮成形、射出成形、押出成形、コーティング等のいずれでもよい。

【0019】

乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンスポンジゴム成形体は、乳化剤と水溶性ポリマーを含有する付加反応硬化型シリコーンゴム組成物、好ましくは付加反応硬化型液状シリコーンゴム組成物を硬化させることによって製造することができる。

【0020】

かくして得られたシリコーンスポンジゴム成形体は乳化剤と水溶性ポリマーを含有するので、水性樹脂をはじき難いという特徴があり、水性樹脂の塗工が容易である。水性樹脂は、水に分散、乳化または溶解した有機樹脂、好ましくは硬化性有機樹脂であり、加熱するか、水が蒸発すると強固な皮膜を形成するものである。なかでも、分子中に親水性基を有

し、水中に微粒子がコロイド状に分散しており、乳化剤を含有しないものが好ましい。具体的には水性ウレタン系樹脂、水性アクリル系樹脂、水性ポリエステル樹脂、水性エポキシ樹脂、水性フッ素樹脂、水性シリコン樹脂、水性ポリエチレン樹脂、特にこれら硬化性水性樹脂が例示されるが、水性ウレタン系樹脂の皮膜はゴム弾性を有しており、機械的強度が優れているので最も好ましく、ついで水性アクリル系樹脂、水性フッ素樹脂が好ましい。これら水性樹脂は、水分が蒸発すると強固な皮膜を形成するもの、特殊官能基で変性されており自己架橋するもの、架橋剤と混合すると架橋して硬化するもの、硬化触媒と混合すると架橋して硬化するものなどがある。必要に応じて架橋剤および／または硬化触媒が配合され、さらには接着性付与剤、着色剤、難燃剤、防腐剤、防黴剤、少量の有機溶媒などが配合されてもよい。

#### 【0021】

水性樹脂のシリコンスポンジゴム成形体への塗布は、含浸、噴霧塗装、刷け塗り、ローラーコーティング、ナイフコーティングなど種々の方法をとることができる。水性樹脂の塗布量は、室温での風乾後、または加熱乾燥後の皮膜厚さが $5\mu\text{m}$ ～ $70\mu\text{m}$ の範囲となるような量が好ましい。水性樹脂の弾性率によって異なるが、水性樹脂からの樹脂膜の膜厚が $5\mu\text{m}$ ～ $100\mu\text{m}$ の範囲であれば、シリコンスポンジゴム成形体の柔軟性を損なうことがない。水性樹脂からの樹脂膜、好ましくは硬化樹脂膜はシリコンスポンジゴム成形体の全面または一部の面に積層されている。一部の面の一部に積層されていてもよい。

#### 【実施例】

#### 【0022】

以下、本発明の実施例と比較例を掲げる。実施例と比較例中、部とあるのは重量部のことであり、％とあるのは重量％のことであり、粘度は $25^{\circ}\text{C}$ での数値を示す。なお、本発明は、これらの実施例によって限定されるものではない。

#### 【0023】

実施例と比較例中の各特性は下記の条件で測定した。

シリコンスポンジゴムの密度：シリコンスポンジゴムシートを一定直径のボンチで打ち抜き、その打ち抜いたシート片の重量と厚みを測定して、重量／体積( $\text{g}/\text{cm}^3$ )を密度として算出した。

水性樹脂のハジキ：シリコンスポンジゴムのダンベル片を水性樹脂に浸漬し、取り出した時のハジキを目視で観察した。

シリコンスポンジゴムの硬さ：JIS K6253にしたがい、ゴム硬度計用低圧加重器CL-150(高分子計器株式会社製)を用いて測定した。

シリコンスポンジゴムの引張強さ：JIS K6251にしたがって測定した。

樹脂皮膜を有するシリコンスポンジゴムの摩耗率：スガ磨耗試験機NUS-ISO-1(スガ試験機株式会社製)を使用して、往復運動磨耗試験法によって測定した。粒度1200の研磨紙を貼り付けた回転ロールを、加重50gとしてシリコンスポンジゴムシート上で30回転させた。(摩耗前試料重量(mg)－摩耗後試料重量(mg)) $\times$ 100／摩耗前試料重量を摩耗率として算出した。なお、摩耗前試料重量は、シリコンスポンジゴムシートの回転ロール接触面積(30mm $\times$ 15mm)と厚さ(約2mm)からなる試験片の重量を測定することにより求めた。

#### 【0024】

実施例と比較例で使用した成分は下記のとおりである。

A-1：粘度10,000mPa・sの分子鎖両末端がジメチルビニルシロキシ基で封鎖されたジメチルポリシロキサン(ビニル基含有量0.14%)100部とヘキサメチルジシラザンで表面処理された比表面積200m<sup>2</sup>/gの疎水性ヒュームドシリカ17部を均一に混合し、180 $^{\circ}\text{C}$ で2時間熱処理を行って調製された、流動性のある液状シリコンゴムベース；

A-2：粘度40,000mPa・sの分子鎖両末端がトリメチルシロキシ基で封鎖されたジメチルシロキサン・メチルビニルシロキサンコポリマー(ビニル基含有量0.14%)100部とジメチルジクロロシランで表面処理されたヒュームドシリカであるアエロ

ジルR-972(日本アエロジル株式会社製)17部を均一に混合し、180℃で2時間熱処理を行って調製された、流動性のある液状シリコーンゴムベース;

B:粘度5mPa・sの両末端トリメチルシロキシ基封鎖ジメチルシロキサン・メチルハイドロジェンシロキサンコポリマー(ケイ素原子結合水素含有量0.8%);

C:塩化白金酸とジビニルテトラメチルジシロキサンとの錯体;

D:付加反応抑止剤としての3,5-ジメチル-1-ヘキシン-3オール;

E-1:水溶性ポリマーであるポリアクリル酸ナトリウムの水溶液(水溶性ポリマー含有量1%);

E-2:水溶性ポリマーであるカルボキシメチルセルロースのナトリウム塩の水溶液(水溶性ポリマー含有量3%);

E-3:吸水性ポリマーであるアクリル酸塩重合体部分ナトリウム塩架橋物でゲル化させた水(吸水性ポリマー含有量0.3%);

E-4:イオン交換水

F-1:ポリオキシエチレンジオレエート(HLB値10.4);

F-2:ポリオキシエチレンジラウレート(HLB値6.6);

F-3:ポリオキシエチレンラウリルエーテル(HLB値9.6);

F-4:高級アルコール系非イオン系界面活性剤サンノックSS-50(HLB値10.5)(三洋化成工業株式会社製);

F-5:高級アルコール系非イオン系界面活性剤サンノックSS-70(HLB値12.8)(三洋化成工業株式会社製);

G:水性ポリエステル系ウレタン樹脂「ハイドランHW-311」(イオン性を有するウレタン樹脂、すなわち、ウレタンアイオノマーがその親水性であるイオン基により水中に溶解しない極めて微粒子状に分散した、いわゆるコロイド分散型の水性ウレタン樹脂。組成:ウレタン樹脂44%~46%、トリエチルアミン1~2%、水52~54%。pH:7.8~8.8、イオン性:アニオン性、皮膜特性:100%モデュラス27kgf/cm<sup>2</sup>、軟化温度80~90℃。大日本インキ化学工業株式会社製);

H:水性ポリエーテルポリエーテル系ウレタン樹脂「バインダーCB-556」(組成:ポリエーテルポリエーテル系ウレタン樹脂35%~45%、ポリエチレングリコールモノ(またはジ)脂肪酸(8~38)エステル(n>100)、pH:弱アルカリ性、イオン性:アニオン性、皮膜:弾力性、耐水性、耐溶剤性が優れている。林化学工業株式会社製)をイオン交換水で2倍に希釈したもの;

I:アクリル樹脂エマルジョン「VONCOAT OC-119H」(不揮発分39%、粘度1000~5000mPa・s、粒子荷電:アニオン、皮膜特性:Tg10℃、100%モデュラス7.9MPa、抗張力18MPa、大日本インキ化学工業株式会社製);

J:カルボキシル基含有ポリエチレン系樹脂エマルジョン「ベターゾル」(エチレンアクリル酸共重合体樹脂を主成分とし、架橋剤と諸物性付与剤を配合したソープフリーコロイド状エマルジョン。半透明ゾル状液。固形分20%、粘度500cP以下、pH7~11、液比重1.0~1.1、粒径0.07μm、水分蒸発後、架橋構造を持った水不溶性皮膜を形成する。皮膜硬さ2H、株式会社セイシン企業製);

K:水性フッ素樹脂「ダイエルラテックスGLS-213CR」(組成:フッ素ゴム20~30%、フッ素樹脂20~30%、ポリオキシエチレン=オクチルフェニルエーテル2.2%、水40~50%、pH:8~10、硬化温度:120~350℃、粘度:50~130mPa・s、皮膜:非粘着性、潤滑性に優れている。ダイキン工業株式会社製)

【0025】

【実施例1】

A-1の100部にE-1の100部、F-1の0.5部、F-2の2部を加えて、T.K.ホモキサーMARKII2.5型(特殊機化工業株式会社製)を使用して、5,000rpmで5分間攪拌混合して、水性エマルジョンを調製した。

次に、この水性エマルジョンに、表1の配合比でB、C、Dそれぞれを加えて攪拌混合し、真空ポンプで脱気した。次に、脱気したそれぞれの試料を厚さ2mmのシート状金型に流し込み、加圧下で90℃、10分間かけて硬化させ、得られたシリコーンゴムスポンジ様シートを150℃の熱風循環式オーブンに入れ、1時間かけて熱風乾燥して、シート状のシリコーンスポンジゴムを得た。このシリコーンスポンジゴムを3号ダンベルで打ち抜き、ダンベル片を各水性樹脂G、H、I、J、Kに浸漬してハジキの状況を観察して、その結果を表1に示した。この結果から、本発明によるシリコーンスポンジゴム成形体は水性樹脂のハジキが無く、樹脂皮膜を均一に形成できることが判った。

【0026】

〔実施例2〕

A-1の100部にE-1の50部、E-2の50部、F-1の0.5部、F-2の2部を加えて、実施例1と同一条件で水性シリコーンエマルジョンを調製した。次に、この水性シリコーンエマルジョンに、表1の配合比でB、C、Dそれぞれを加えて攪拌混合し、実施例1と同一の手順でシート状のシリコーンスポンジゴムを作製した。実施例1と同一の方法でハジキの観察をおこない、その結果を表1に示した。

【0027】

〔比較例1〕

A-1の100部に、E-3の100部、F-3の5部を加えて、実施例1と同一条件で水性シリコーンエマルジョンを調製した。次に、表1の配合比でB、C、Dそれぞれを加えて攪拌混合し、実施例1と同一の手順でシート状のシリコーンスポンジゴムを作製した。不均一セルの3号ダンベル片で水性樹脂に対するハジキを調べて表1に示した。ハジキのため均一な樹脂皮膜形成は困難であった。

【0028】

〔比較例2〕

A-1の100部に、E-3の100部、F-1の0.5部、F-2の2部を加えて、実施例1と同様な手順でエマルジョンを作製し、次に、実施例1と同様な手順でシリコーンスポンジゴムシートを作製し、3号ダンベル片で水性樹脂に対するハジキを調べて表1に示した。ハジキのため均一な樹脂皮膜形成は困難であった。

【0029】

〔比較例3〕

A-1の100部に、E-3の50部、F-1の1.0部を加えて、実施例1と同様な手順でエマルジョンを作製し、次に、実施例1と同様な手順で不均一セルのシリコーンスポンジゴムシートを作製し、3号ダンベル片で水性樹脂に対するハジキを調べて表1に示した。ハジキのため均一な樹脂皮膜形成は困難であった。

【0030】

〔比較例4〕

A-1の100部に、E-4の50部、F-1の5.0部を加えて、実施例1と同様な手順でエマルジョンを作製し、次に、実施例1と同様な手順でシリコーンスポンジゴムシートを作製し、3号ダンベル片で水性樹脂に対するハジキを調べて表1に示した。ハジキのため均一な樹脂皮膜形成は困難であった。

【0031】

〔実施例3〕

実施例1と同一条件で水性シリコーンエマルジョンを調製した。次に、表2の配合比でそれぞれB、C、Dを加えて攪拌混合し、実施例1と同一の手順でシート状のシリコーンスポンジゴムを作製した。このシリコーンスポンジゴムを3号ダンベルで打ち抜き、Gに浸漬させた後、110℃の熱風式オーブンに10分間入れ、その後室温で20時間かけて乾燥して、均一な表2に示す膜圧を有する樹脂皮膜を形成させた。この樹脂皮膜を有するシリコーンスポンジゴムの引張強さと摩耗率を測定して表2に示した。この結果から、本発明による均一な樹脂皮膜を有するシリコーンスポンジゴムは高い機械強度と耐摩耗性を有することがわかる。

【0032】

〔実施例4〕

A-1の100部にE-1の50部、E-2の50部、F-1の0.5部を加えて、実施例1と同一条件で水性シリコンエマルジョンを調製した。次に、このエマルジョンに、表2の配合比でB、C、Dそれぞれを加えて攪拌混合し、実施例1と同一の手順でシート状のシリコンスポンジゴムを作製した。このシリコンスポンジゴムを3号ダンベルで打ち抜き、Hに浸漬し、実施例3と同一の乾燥条件で乾燥して、均一な表2に示す膜厚を有する樹脂皮膜を形成させた。この樹脂皮膜を有するシリコンスポンジゴムの引張強さと摩耗率を測定して、表2に示した。

【0033】

〔実施例5〕

A-2の100部にE-2の100部、F-4の2.0部、F-5の2.0部を加えて、実施例1と同一条件で水性シリコンエマルジョンを調製した。次に、このエマルジョンに表2の配合比でB、C、Dそれぞれを加えて攪拌混合し、実施例1と同一条件でシート状のシリコンスポンジゴムを作製した。このシリコンスポンジゴムを3号ダンベルで打ち抜き、Hに浸漬し、実施例3と同一の乾燥条件で乾燥して、均一な表2に示す膜厚を有する樹脂皮膜を形成させた。この樹脂皮膜を有するシリコンスポンジゴムの引張強さと摩耗率を測定して、表2に示した。

【0034】

〔比較例5〕

実施例3で作製したシート状のシリコンスポンジゴム（水性樹脂の皮膜を有しない）の密度、硬さ、引張強さ、摩耗率を測定して、表3に示した。

【0035】

〔比較例6〕

実施例4で作製したシート状シリコンスポンジゴム（水性樹脂の皮膜を有しない）の密度、硬さ、引張強さ、摩耗率を測定して、表3に示した。

【0036】

〔比較例7〕

実施例5で作製したシート状シリコンスポンジゴム（水性樹脂の皮膜を有しない）の密度、硬さ、引張強さ、摩耗率を測定して、表3に示した。

【0037】



【表1】

## 水性樹脂のハジキ

	実施例1	実施例2	比較例1	比較例2	比較例3	比較例4
A-1	100	100	100	100	100	100
B	0.5	1.5	1.5	1.5	1.5	1.5
C	0.3	0.3	0.3	0.3	0.3	0.3
D	0.01	0.01	0.01	0.01	0.01	0.01
E-1	100	50				
E-2		50				
E-3			100	100	50	
E-4						50
F-1	0.5	0.5		0.5	1.0	5
F-2	2.0	2.0		2.0		
F-3			5			
G	無し	無し	有り	有り	有り	有り
H	無し	無し	有り	有り	有り	有り
I	無し	無し	有り	有り	有り	有り
J	無し	無し	有り	有り	有り	有り
K	無し	無し	有り	有り	有り	有り

【0038】

【表2】

水性樹脂皮膜の特性

	実施例3	実施例4	実施例5
A-1	100	100	
A-2			100
B	1.5	1.5	1.0
C	0.3	0.3	0.3
D	0.01	0.01	0.01
E-1	100	50	
E-2		50	100
F-1	0.5	0.5	
F-2	2.0		
F-4			2.0
F-5			2.0
G膜厚(μm)	50		
H膜厚(μm)		20	20
密度(g/cm <sup>3</sup> )	—	—	—
硬さ	—	—	—
引張強さ(MPa)	0.32	0.29	0.12
摩耗率(%)	7.0	3.7	13.1

【0039】

【表3】

水性樹脂皮膜の特性

	比較例5	比較例6	比較例7
A-1	100	100	
A-2			100
B	1.5	1.5	1.0
C	0.3	0.3	0.3
D	0.01	0.01	0.01
E-1	100	50	
E-2		50	100
F-1	0.5	0.5	
F-2	2.0		
F-4			2.0
F-5			2.0
G膜厚 ( $\mu\text{m}$ )	—	—	—
H膜厚 ( $\mu\text{m}$ )	—	—	—
密度 ( $\text{g}/\text{cm}^3$ )	0.61	0.60	0.60
硬さ	14	30	18
引張強さ (MPa)	0.15	0.24	0.04
摩耗率 (%)	15.4	34.8	40.3

【産業上の利用可能性】

【0040】

本発明の樹脂皮膜を有するシリコーンスポンジゴム成形体は、織物や不織布のコーティング膜、硝子クロスのコーティング膜、断熱シート、クッション、パッキング、定形シール材などとして有用である。本発明の樹脂皮膜を有するシリコーンスポンジゴム成形体の製造方法は、樹脂皮膜を有するシリコーンスポンジゴム成形体を効率、生産性よく製造するのに有用である。

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